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Orientation of Anthracene in Stretched Polyvinylchloride

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Dichroic measurements were made of anthracene in polyvinylchloride films stretched at various degree of elongation. A band at 363 nm of anthracene shows parallel dichroism at small elongation, but perpendicular at large elongation. This change of dichroism was theoretically interpreted. The results indicate that the long axis and the plane of the anthracene molecule orients predominantly parallel to the stretching direction.

INTRODUCTION

Many studies¹⁻⁴⁾ have been made of orientation of small molecules dispersed in stretched polymer films, and of interactions between them. Umemura, Takenaka, Hayashi, and Gotoh⁵⁾ measured differential polarized infrared spectra of polyvinylchloride (PVC) films containing dioctyl phthalate or diethyl phthalate and discussed the effect of concentration of the plasticizer on orientation. Kobayashi, Okajima, and Nakayama⁶⁾ utilized visible dichroism of dye molecules as a measure of the degree of polymer orientation.

We have previously measured dichroism of absorptions of anthracene dispersed in PVC film by means of a spectropolarimeter at a limited degree of elongation (80%) of the film, and estimated the orientation function of the short axis of anthracene and that of the CH₂ group of PVC.⁷⁾ After the publication of the previous work, a band at 363 nm is found to show parallel dichroism at the limited degree of elongation, however, perpendicular dichroism at large degree of elongation. Inoue, Hoshi, Masamoto, Shiraishi, and Tanizaki have also measured polarized spectra of anthracene dispersed in stretched polyvinylalcohol.⁸⁾ Their spectra were analyzed using a theory proposed by Tanizaki who discussed the dichroic ratio as a function of degree of elongation.⁹⁾ However, the theory could not interpret the change of dichroism from parallel to perpendicular.

In this work, the change of dichroism from parallel to perpendicular polarization and details of the orientation of the anthracene and PVC molecules were discussed in a wide range of elongation (500%).

EXPERIMENTAL

Materials

The polymer used in this study was commercially available polyvinylchloride. Zonerefined anthracene and cyclohexanone of spectroscopic grade (Tokyo Kasei Co., Ltd) were used without further purification. The film sample was prepared by casting from a cyclohexanone solution of anthracene and polyvinylchloride at room temperatures.

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Before use, the film was washed by a mixed solvent of alcohol and water at 70°C for one hour, and then dried at 90°C for three hours in a dry box. The film has no absorption due to the solvent at 280 nm, and has thickness of about 40 μ . A rectangular strip (2.4 \times 4.0 cm) of the film was stretched to various length in hot water (90°C).

Measurements

The measurements of the polarized spectra in the ultraviolet and visible region were carried out by a Hitachi EPS-3 spectrophotometer equipped with a Glan-Thomson type polarizer, and those in the infrared region were observed by a Perkin-Elmer model 521 spectrophotometer equipped with a wire-grid polarizer.

INTERPRETATION OF SPECTRA

Since infrared absorption bands of anthracene in the PVC films were very weak, the orientation of the molecules was discussed by dichroic measurements of ultraviolet absorption bands. On the other hand, PVC is transparent in the ultraviolet region, but has many bands in infrared region. Orientation of PVC was estimated by an infrared band at 1426 cm^{-1} .

Interpretation of the spectrum of anthracene has been given by many workers using quantum mechanical and experimental method.¹⁰⁻¹⁵⁾ The 257-nm band, the most intense band in the spectrum of anthracene, has been assigned to the 1B_b band, due to ${}^1B_{1u} \leftarrow {}^1A_g$ transition. This transition is polarized in the direction of the long axis of the molecule. The band at 383 nm has been assigned to the 1L_a band due to ${}^1B_{2u} \leftarrow {}^1A_g$ transition, and polarized parallel to the short axis. The several bands in the 300–370 nm region have been interpreted as superposition of the bands due to the transition polarized in the short-axis direction (1L_a) upon those due to the other transition polarized in the long-axis direction (1L_b).^{16,17)}

The infrared band at 1426 cm^{-1} has been assigned to the bending mode of the CH_2 group in the syndiotactic trans-trans configuration. The direction of the transition moment could be considered to be nearly perpendicular to the polymer chain.^{5,18)}

THEORY

The relative position of space (X, Y, Z) and molecular (x, y, z) coordinate systems is shown in Fig. 1. The direction of propagation of the incident light is chosen parallel to the Z axis, and the plane of the film coincides with the XY -plane. The angles θ and ϕ are those formed by the Y axis against the x and y axes, respectively, and γ and δ are the angles formed by the X axis against the projection of the x and y axes to the XZ plane, respectively.

The molar extinction coefficients at a given wavelength (λ) along the long and short axes of the molecule (K_l^2 and K_s^2 , respectively) are related with the optical densities, A_l^2 and A_s^2 which are observed by the plane-polarized light with the electric vectors parallel to the Y and X axes, respectively.

$$A_l^2 = (K_l^2 \cos^2 \theta + K_s^2 \cos^2 \phi) C d \quad (1)$$

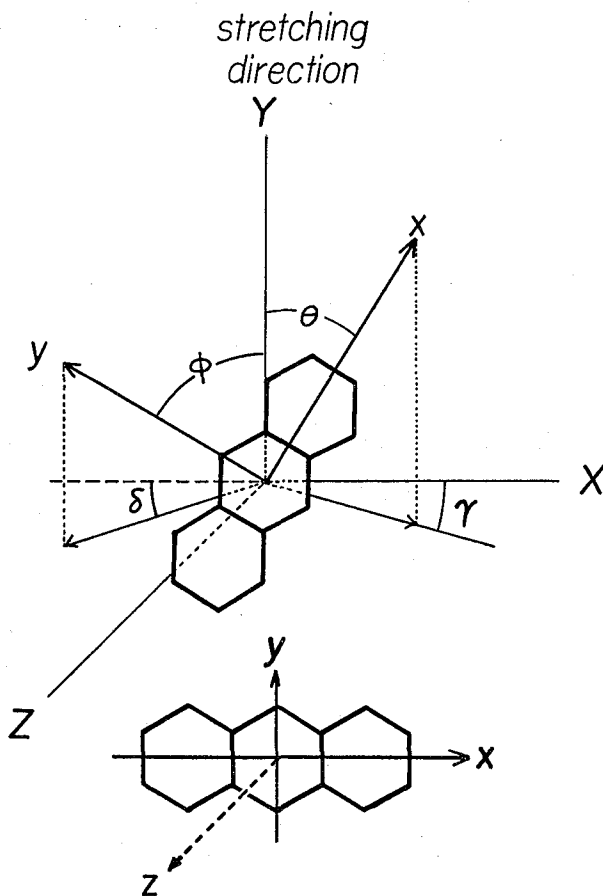


Fig. 1. Coordinate system used for describing a uniaxial orientation of anthracene.

$$A_{\perp}^2 = \frac{1}{2} (K_l^2 \overline{\sin^2 \theta} + K_s^2 \overline{\sin^2 \phi}) C d \quad (2)$$

where C and d are the concentration and the thickness of the film, respectively. The coefficient $1/2$ in Eq. (2) is obtained by integrating the component of transition moment in the X direction over the angle γ . The averages of the direction cosines are given by

$$\overline{\cos^2 \theta} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \cos^2 \theta \sin \theta \, d\theta \, d\gamma \quad (3a)$$

$$\overline{\cos^2 \phi} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \cos^2 \phi \sin \theta \, d\theta \, d\gamma \quad (3b)$$

$$\overline{\sin^2 \theta} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \sin^2 \theta \sin \theta \, d\theta \, d\gamma \quad (3c)$$

$$\overline{\sin^2 \phi} = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} \sin^2 \phi \sin \theta \, d\theta \, d\gamma \quad (3d)$$

If the transition moments of bands at 257 and 383 nm are parallel to the long and the

short axes, respectively, the orientation functions of these axes of the molecule, F_l and F_s , may be expressed by the absorbances A_l^{λ} and A_{\perp}^{λ} .

$$F_l = \frac{1}{2}(3\overline{\cos^2\theta} - 1) = \frac{A_l^{257} - A_{\perp}^{257}}{A_l^{257} + 2A_{\perp}^{257}} \quad (4)$$

$$F_s = \frac{1}{2}(3\overline{\cos^2\phi} - 1) = \frac{A_l^{383} - A_{\perp}^{383}}{A_l^{383} + 2A_{\perp}^{383}} \quad (5)$$

The orientation function of the direction perpendicular to the molecular plane (F_p) with respect to the stretching direction can be obtained from the following relation.

$$F_p = -(F_l + F_s) \quad (6)$$

The quantity $(A_l^{\lambda} - A_{\perp}^{\lambda})/(A_l^{\lambda} + 2A_{\perp}^{\lambda})$ at a given wavelength (λ) is used for a representation of dichroism, and is related with the orientation functions of the molecule.

$$\frac{A_l^{\lambda} - A_{\perp}^{\lambda}}{A_l^{\lambda} + 2A_{\perp}^{\lambda}} = \frac{K_l^{\lambda}(\overline{\cos^2\theta} - 1/2 \overline{\sin^2\theta}) + K_s^{\lambda}(\overline{\cos^2\phi} - 1/2 \overline{\sin^2\phi})}{K_l^{\lambda} + K_s^{\lambda}} \quad (7)$$

$$= aF_l + bF_s \quad (8)$$

where the parameters a and b denote the ratios of the molar extinction coefficient for the long and short axes, respectively, to the total molar extinction coefficient in an absorption at wavelength λ .

$$a = \frac{K_l^{\lambda}}{K_l^{\lambda} + K_s^{\lambda}}, \quad b = \frac{K_s^{\lambda}}{K_l^{\lambda} + K_s^{\lambda}} \quad (9)$$

RESULTS AND DISCUSSION

Figure 2 illustrates the absorption spectrum of anthracene dispersed in PVC film. This spectrum is similar to that in various solutions of low concentration but is different from that in the crystalline^{14,19,20} or gaseous states.^{21,22} It may be considered that the anthracene molecules are monomolecularly dispersed in PVC film.

Orientation of Polyvinylchloride

The degrees of orientations of the PVC molecules are estimated from the dichroism of

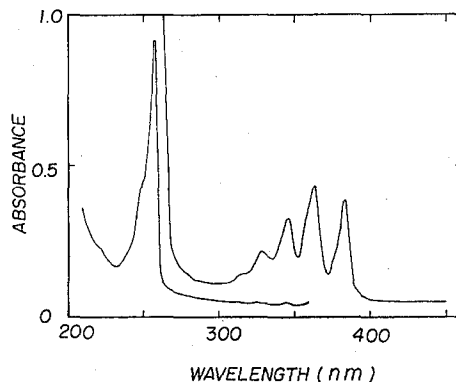


Fig. 2. Ultraviolet absorption spectrum of anthracene dispersed in PVC film.

Orientation of Anthracene in PVC

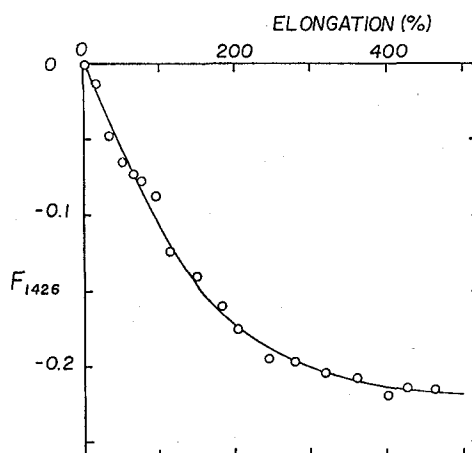


Fig. 3. Variation of the orientation function of PVC (for 1426 cm^{-1} band) with percent elongation.

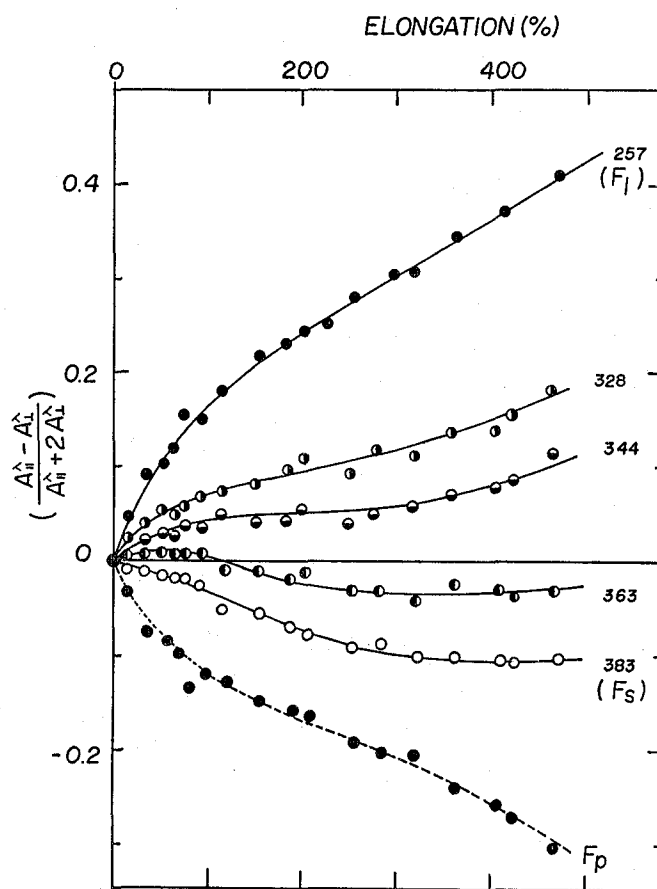


Fig. 4. Variation of the orientation functions for each band of anthracene with percent elongation.

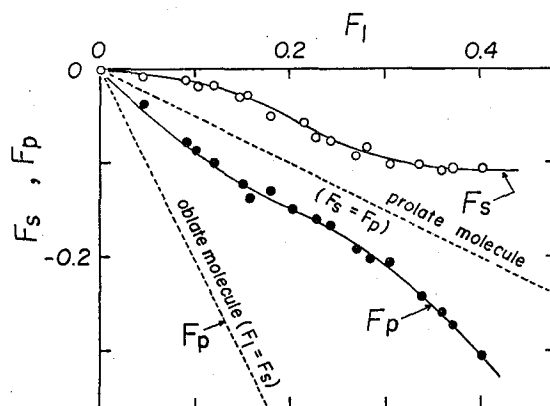


Fig. 5. Relation between the orientation functions F_I and F_S or F_P . See the text about theoretical lines for prolate and oblate molecules.

the infrared band at 1426 cm^{-1} which has been assigned to the bending mode of the CH_2 group in the syndiotactic trans-trans conformation.⁵⁾ The direction of the transition moment of this band is considered to be nearly perpendicular to the polymer chain. The orientation function of the CH_2 group decreases smoothly with elongation until a value about -0.22 as shown in Fig. 3. This indicates that the PVC molecular chain orients to the stretching direction.

Orientation of Anthracene

The orientation functions of the long and short axes of the anthracene molecule are estimated from the dichroism of the bands at 257 and 383 nm as described above. The orientation function of the long axis of anthracene increases with the elongation, while that of the short axis decreases as shown in Fig. 4.

The orientation function of the direction perpendicular to the molecular plane (F_P)

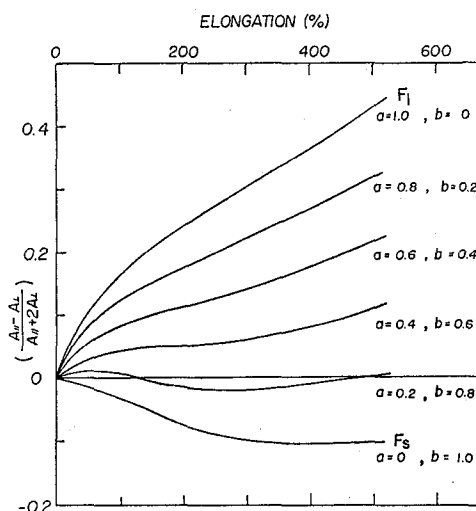


Fig. 6. Calculated variation of the orientation function with the elongation for various values of the parameters a and b .

is also shown in Fig. 4, and is smaller than F_s .

In Fig. 5, the values of F_l at various degrees of elongation are plotted against the corresponding values of F_s and F_p . The theoretical curves for prolate and oblate molecules are also given in Fig. 5. The former has two equivalent short axes and one long axis. The line for this molecule is expressed by the equation, $F_l = -2F_p(F_s = F_p)$, and means that the long axis of the molecule orients to the stretching direction. The latter has two equivalent long axes and one short axis. The line for this model is given by the equation, $F_l = -1/2 \cdot F_p(F_s = F_l)$, and denotes that the plane of the molecule orients to the stretching direction. Comparison of the theoretical lines with the experimental curve shows that the behavior of the anthracene molecule is intermediate between the prolate and oblate molecules, and that the long axis and the plane of the molecule orient predominantly parallel to the stretching direction at the same time, and the short axis orients perpendicular to the direction.

Figure 4 shows the quantities $(A_l^2 - A_{\perp}^2)/(A_l^2 + 2A_{\perp}^2)$ for 328, 344, and 363-nm bands which have both components for the long axis transition and for the short axis transition. It can be seen that the value for the 363-nm band changes from positive to negative with the elongation.

The values of $(A_l^2 - A_{\perp}^2)/(A_l^2 + 2A_{\perp}^2)$ are calculated from Eq. (8) with various values of the parameters a and b , and are shown in Fig. 6, in which the experimental results for F_l and F_s are used. This figure may interpret satisfactorily the experimental results, especially, the change of the orientation function for the 363-nm band, and gives the values of the parameters a and b for anthracene bands. The results are listed in Table I.

Interaction between Anthracene and PVC

Figure 7 is the relation between the orientation function of the anthracene band at 257

Table I. The Parameters a and b of Each Band of Anthracene

wavelength (nm)	257*	328	344	363	383*
a	1.00	0.54	0.39	0.15	0
b	0	0.46	0.61	0.85	1.00

* see the text

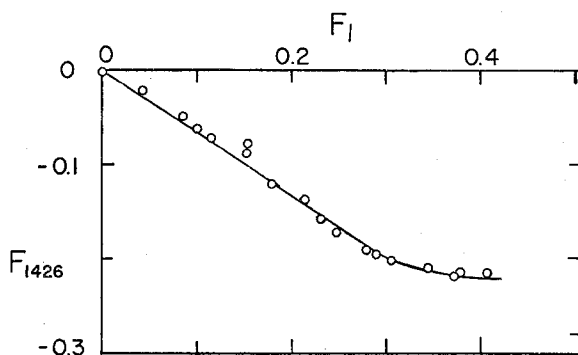


Fig. 7. Relation between the orientation functions F_{1426} and F_l .

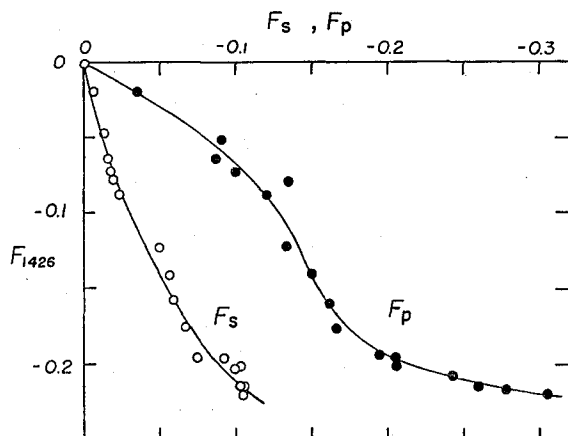


Fig. 8. Relation between the orientation functions F_{1426} and F_s or F_p .

nm and that of the PVC band at 1426 cm^{-1} . A linear relation is obtained until the point $F_l=0.3$ and $F_{1426}=-0.2$. Over the point, F_l increases, but F_{1426} is nearly constant.

Figure 8 illustrates the variations of F_s and F_p against F_{1426} . F_s decreases monotonously with F_{1426} and stops the progress at the values of -0.1 of F_s and of -0.22 of F_{1426} . While F_p decreases with the elongation of the film even after stopping the progress for F_{1426} .

If anthracene molecules are bound strongly with the PVC polymer, the orientation of anthracene molecule should change linearly to that of the PVC in the whole range of elongation. However, the experimental results do not show the linear relationship. Therefore, we thought that intermolecular forces between anthracene and PVC must be weak, and that the PVC molecule could slip keeping a constant orientation when rubber elasticity of the polymer overcomes intermolecular forces, and orientation of the anthracene molecules could increase even when the polymer is slipping.

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